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TRANSLATION

DERIVATIVES OF PERFLUODICARBONIC ACIDS

By

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DERIVATIVES OF PERFLUODICARBONIC ACIDS

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In a report published previously [1] there is a description of obtaining higher perfluodicarbonic acids by the oxidation of α, ω-perfluodiolefins:

$$CF_2=CF-(CF_2)_n-CF=CF_2 \xrightarrow{KMnO_4} HOOC-(CF_2)_n-COOH \qquad (1)$$
$$n=4,8,12 \qquad\qquad n=4,8,12$$

In continuing the work in the synthesis and use of perfluodicarbonic acids we prepared some bifunctional derivatives of perfluoradipic, perfluosebacic, and perfluododeca-methylene-dicarbonic acids obtained by oxidation of perfluoroctadiene, perfluododecadiene, and perfluohexadecadiene, respectively. There were prepared chloranhydrides, esters, amides, nitriles, and amidines of the acids indicated by the following procedure:

$$\begin{array}{l} HOOC-(CF_2)_n-COOH \xrightarrow[FSO_3H]{C_2H_5OH} C_2H_5OCO-(CF_2)_n COOC_2H_5 \xrightarrow{NH_3} H_2NCO(CF_2)_n CONH_2 \\ \quad \Big\downarrow \begin{matrix} SOCl_2 \\ KCl \end{matrix} \quad n=4,8,12 \qquad\qquad\qquad\qquad\qquad\qquad \Big\downarrow P_2O_5 \\ ClCO(CF_2)_n COCl \quad HN=C-(CF_2)_n-C=NH \xleftarrow{m\cdot NH_3} N\equiv C-(CF_2)_n-C\equiv N \\ \qquad\qquad\qquad\quad NH_2 \qquad\qquad NH_2 \end{array} \qquad (2)$$

From the same perfluodicarbonic acids—perfluoradipic, perfluosebacic, and perfluododeca-methylene-dicarbonic—through the reduction of their ethyl esters by sodium borohydride in diglyme in the presence of anhydrous ammonium chloride [2] there were synthesized the respective $\alpha, \alpha, \omega, \omega$-tetrahydroperfluodiols:

$$C_2H_5OCO-(CF_2)_n COOC_2H_5 \xrightarrow[\text{диглим}]{NaBH_4, AlCl_3} HOCH_2-(CF_2)_n CH_2OH \qquad (3)$$
$$n=4,8,12$$

The method of reduction of the sodium borohydride was taken by us for the first time for the reduction of esters of perfluodicarbonic acids, and it showed a number of advantages over reduction by lithium-aluminum-hydride in ether solutions [3].

Some bifunctional derivatives of perfluodicarbonic acids; for example, amidines and $\alpha, \alpha, \omega, \omega$-tetrahydro-perfluodiols, were used for obtaining polymer compounds.

Experimental Part

Obtaining derivatives of perfluodicarbonic acids Esters. 0.05 of a mole of perfluodicarbonic acid are dissolved in 30 to 50 ml of abs ethanol, there is added 1.5 ml of fluosulfonic acid, and the whole is heated in a boiling-water bath for 1.5 hours. The solution is poured into cold water, and the flaked oil is taken into ether, washed with a solution of $NaHCO_2$ and water, dried and distilled. One gets diethyl esters: of perfluoradipic acid, b. p. 96—97°/7 mm, n_D^{20} 1.3541, d_4^{20} 1.426, yield 90%; perfluosebacic acid, b. p. 118—120°/5 mm, n_D^{20} 1.3424, d_4^{20} 1.578, yield 95%; perfluododeca-methylene-dicarbonic acid, b. p. 142—143°/5 mm, n_D^{20} 1.3408, d_D^{20} 1.686, yield 70%. There were found %: C 28.22; H 1.14; F 61.83; $C_{18}H_{10}O_4F_{24}$. Computed %: C 28.95; H 1.34; F 61.12.

Chloranhydrides. 0.02 of a mole of perfluodicarbonic acid are mixed with 0.08 to 0.1 of a mole of $SOCl_2$, there is added 0.01 of a mole of KOH and 2 to 3 drops of pyridine, and the whole is heated in a boiling-water bath for several hours (until complete solution of the acid). The excess of $SOCl_2$ is evaporated out and the product of the reaction is distilled. One gets chloranhydrides: of perfluoradipic acid, b. p. 130—132°, n_D^{20} 1.3484, yield 78%, perfluosebacic acid, B. P. 115--117°/40 mm, m. p. 29—30°, yield 78%; perfluododeca-methylene-dicarbonic acid, b. p. 161°/50 mm, m. p. 92—95°, yield 74%. There were found %: C 23.37; F 61.84; $C_{14}O_2F_{24}Cl_2$. Computed %: C 23.10, F 62.72.

Amides. 0.05 of a mole of ethyl esters of perfluodicarbonic acid are dissolved in 50 to 60 ml of abs. ester, and a current of dry NH_3 is passed through until saturation. One gets amides of perfluodicarbonic acids with a yield of 95—98%: amide of perfluoradipic acid, m. p. 235 to 238°, amide of perfluosebacic acid, m. p. 238--239°; amide of perfluododeca-methylene-

dicarbonic acid, m. p. 242—244°. There were found %: C 24.01; H 0.72; F 66.41; N 3.48; $C_{14}H_4O_2F_{24}N_2$. Computed %: C 24.41; H 0.59; N 4.07; F 66.28.

Nitriles. 0.02—0.05 of a mole of amide of perfluodicarbonic acid is mixed with 0.1—of a mole of P_2O_5 and heated in Wood's bath at 100—300° with simultaneous evaporation of nitrile being formed. In obtaining the nitrile of perfluododeca-methylene-dicarbonic acid the evaporation is done in a vacuum. The nitriles obtained are distilled once more: nitrile of perfluoradipic acid, b. p. 63°, yield 77%; nitril of fluosebacid acid, b. p. 147—148°, n_D^{20} 1.3039, d = 1.673, yield 80%. There were found %: C 26.10; F 67.63; N 6.70; $C_{10}F_{16}N_2$. Computed %: C 26.54; F 67.25; N 6.19; nitril of perfluododeca-methylene-dicarbonic acid, b. p. 115—120°/10 mm, m. p. 78 (from acetone). There were found %: C 26.08; F 69.25 N 4.34; $C_{14}F_{24}N_2$.

Amidines. 0.02—0.05 of a mole of perfluodicarbonic acid are placed in a two-necked retort with a reverse cooler for dry ice (CO_2); one adds from a dropping funnel in 2—3 operation 30—40 ml of liquid ammonium, maintains at room temperature for 2 hours, and then leaves for evaporation of the ammonium. In the deposit one gets amidines of perfluodicarbonic acids with a yield of 96—99% in the form of white or yellowish powders. On crystallizes from acetone; one obtains: amidine of perfluoradipic acid, m. p. 154° (literature data [4] 125°). There were found %: C 25.39; H 2.02; F 52.67; N 19. 80; $C_6H_6F_8N_4$. Computed %: C 25.16; H 2.0; F 53.15; N 19.58; amidine of perfluosebacic acid, m. p. 173—175° (with Diff.). There were found %: C 24.40; H 1.40; F 62.12; N 11.02; $C_{10}H_6F_{16}N_4$. Computed %: C 24.69; H 1.23; F 62.55; N 11.52. For obtaining amidine of perfluododeca-methylene-dicarbonic acid a mixture of nitrile and liquid ammonia is kept at room temperature for 10 to 12 hours in a closed steel test tube. After removing the ammonia the amidine dodecamethylene-dicarbonate is washed with acetone

and ether, m. p. 187—190° (with Diff.) There were found %: C 24.20; H 0.94; F 66.60: N 7.96; $C_{14}H_6F_{24}N_{21}$. Computed %: C 24.48; H 0.87; F 66.47; N 8.16.

The obtaining of α, α, ω, ω-tetrahydro-perfluodiols In a three-necked retort with a stirrer, reverse cooler, and a dropping funnel one dissolves 0.04 of a mole of $NaBH_4$ in 25 —30 of dry diglyme (dimethyl ether of diethylene glycol); from the dropping funnel one adds a solution of 0.015 moles of freshly sublimated $AlCl_3$ in 25—30 ml of diglyme and afterwards a solution of 0.02 moles of ethyl ether of perfluodicarbonic acid in diglyme at such a rate that the reaction takes place with moderate cooling. After finishing the addition of the ether one stirs for about 1 hour at room temperature, then while heating in a water bath at 50—60° during the course of 30 to 40 min. After cooling the reaction mixture is gradually transferred to 100 to 200 ml of ice water, made acid by 10 to 15 ml of concentrated hydrochloric acid. The solution obtained goes two or three times through ether extraction. The extract is washed several times with water, dried, and distilled. After evaporation of the ether and a small quantity of diglyme one get crystalline or oil-like residue, which begins to crystallize with the addition of a small amount of chloroform. For final purification of the diols obtained they are distilled in a vacuum or crystallized from $CHCl_3$ or CCl_4. One gets α, α, ω, ω-tetrahydrohexandiol $HOCH_2(CF_2)_4CH_2OH$, b. p. 118—120°/11 mm, m. p. 67—68°, yield 80%; phenylurethane, b. p. 140° (from CCl_4). There were found %: C 48.37; H 3.29; F 31.04: $C_{20}H_{16}F_8O_4N_2$. Computed %: C 48.00; H 3.20; F 30.40; α, α, ω, ω-tetrahydroperfluodecandiol $HOCH_2(CF_2)_8CH_2OH$, b. p. 132°/4 mm; m. p. 135—136°, yield 90%. There were found %: C 25.85; H 1.18; F 68.18; $C_{12}H_6F_{16}O_2$. Computed %: C 25.96; H 1.29, F 67.96, phenylrethane, b. p. 140—141° (from CCl_4). There were found %: C 41.44; H 2.44; F 43.35; N 3.98; $C_{24}H_{16}F_{16}N_2O_4$.

Computed %: C 41.14; H 2.28; F 43.42, M 400, o, o, , -tetrahydroperfluo-tetradecandiol $HOCH_2(CF_2)_{12}CH_2OH$, b. p. 183—184°, yield 87%. There were found %: C 25.27; H 0.93; F 68.68; $C_{14}H_6O_2F_{24}$. Computed %: C 25.37; H 0.90; F 68.88. Phenylurethane, b. p. 153—154°. There were found %: C 37.6[illegible]; H 1.81; F 50.01; $C_{28}H_{16}O_4F_{24}N_2$. Computed %: C 37.33; H 1.7[illegible]; F 50.66.

Conclusions

1. From the above perfluodicarbonic acids of the general formula $HOOC-(CF_2)_nCOOH$, where n = 4, 8, 12 obtained from products of telomerization of tetrafluorethyene by trifluodichloro-iodethane there were synthesized bifunctional derivatives—chloranhydrides, esters, amides, nitriles and amidines.

2. By reduction of esters of perfluoradipic, perfluosebacic, and perfluododeca-methylene-dicarbonic acids using sodium borhydride in the presence of anhydrous ammonium chloride, there were obtained the corresponding α,α,ω,ω-tetrahydroperfluodiols of the general formula $HOCH_2-(CF_2)_nCH_2OH$, where n = 4, 8, 12.

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